BIODEGRADABLE BEHAVIOUR OF POLYLACTIC ACID NANOCOMPOSITE BASED ON MODIFIED NANOCLAY

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ABSTRACT

Polylactic acid (PLA) is a unique polymer. Eventually, this polymer has the broadest range of application especially in biomedical field due to its biocompatibility characteristics. The main purpose of this research is to study on the biodegradable properties of PLA based on modified organoclay. The properties of PLA nanocomposite will be improved by adding nanoclay or Montmorillonite (MMT) and produce PLA nanocomposite. The MMT that used in this research is bis-(2-hydroxyethyl) methyl tallow alkyl ammonium cations (Cloisite B30). A series of PLA nanocomposite was classified by different percentage of compositions and the samples were analysed and compared with pristine PLA. PLA nanocomposite was produced by melt intercalation method using twin screw extruder. Then, the compounds were injection molded by injection molding method and formed dumbbell shape. Meanwhile, PLA nanocomposite is characterized by Scanning Electron Microscopy (SEM) and X–Ray Diffraction Analysis (XRD). However, SEM captures could not determine the dispersion of Cloisite B30 precisely nevertheless it illustrates that aggregates were formed in the images. XRD result supported an exfoliation nanocomposite was possible demonstrated as no diffraction peak was appeared in the XRD results. It also shows that the inter-galleries spacing of the Cloisite B30 between PLA matrixes is too wide. Subsequently, the samples were tested using accelerated weathering tester for biodegradable analysis. Finally, the samples before and after exposed in the accelerated weathering tester were examined by mechanical testing to determine mechanical properties such as ultimate strain, elastic modulus and ultimate stress using tensile strength testing. The most desired result of this research is based on the biodegradable testing. After a year observation, only pristine PLA was sustained in strength while the PLA nanocomposite is so brittle. Meanwhile for a year and half observation, all the samples were so brittle. It can be concluded that the pristine PLA is still remain sustain after a year but it start to degrade after a year and half. The result obtained for before exposing under accelerated weathering tester, the pristine PLA possesses good properties for ultimate strain and ultimate stress rather than elasticity behaviour.

Key words: Polylactic Acid, Polylactic Acid Nanocomposite, Weathering analysis, Biodegradability

ABSTRAK

Polylactic acid (PLA) adalah polimer yang unik. Akhirnya, polimer ini mempunyai kepenggunaan yang luas terutamanya dalam bidang bioperubatan disebabkan oleh ciri–ciri biokeserasiannya. Tujuan utama kajian ini adalah untuk mengkaji sifat-sifat terbiodegradasi PLA berdasarkan tanah liat yang telah diubahsuai. Ciri-ciri nanokomposit PLA akan dipertingkatkan dengan menambah tanah liat yang telah diubahsuai atau montmorilonit (MMT) dan menghasilkan nanokomposit PLA. MMT yang digunakan dalam penyelidikan ini adalah *bis-(2-hydroxyethyl) methyl tallow alkyl ammonium cations* (Cloisite B30). Siri nanokomposit PLA telah diklasifikasikan oleh peratusan komposisi yang berbeza dan sampel dianalisa dan dibandingkan dengan PLA asli. Nanokomposit PLA telah dihasilkan oleh kaedah interkalasi pencairan menggunakan extruder skru berkembar. Kemudian, sebatian dibentuk oleh kaedah pengacuan suntikan dan membentuk bentuk *dumbbell*. Sementara itu, nanokomposit PLA dicirikan oleh *Scanning Electron Microscopy* (SEM) dan *X–Ray Diffraction Analysis* (XRD). Walau bagaimanapun, gambaran dari SEM tidak dapat menentukan penyebaran Cloisite B30 dengan tepat namun ia menunjukkan bahawa agregat telah terbentuk. Keputusan XRD menyokong pengelupasan nanokomposit dengan menunjukkan tiada puncak pembelauan yang muncul dalam keputusan XRD. Ia juga menunjukkan bahawa jarak antara Cloisite B30 antara matriks PLA adalah terlalu luas. Kemudian, sampel telah diuji menggunakan penganalisa cuaca untuk menganalisa siat terbiodegradasi terhadap sampel. Akhir sekali, sampel untuk sebelum dan selepas menggunakan pendedahan penganalisa cuaca telah diperiksa oleh ujian mekanikal untuk menentukan sifat-sifat mekanikal seperti sifat tarikan, modulus kekenyalan dan sifat tekanan menggunakan ujian kekuatan tegangan. Hasil yang paling dikehendaki bagi kajian ini adalah berdasarkan ujian terbiodegradasikan. Selepas setahun pemerhatian, hanya yang PLA asli kekal dengan sifat kekuatannya manakala nanokomposit PLA sangat rapuh. Sementara itu bagi pemerhatian satu tahun enam bulan, semua sampel sangat rapuh. Ia boleh disimpulkan bahawa PLA asli masih kekal sifatnya walaupun selepas setahun tetapi sifatnya mula merosot selepas satu tahun enam bulan. Keputusan yang diperolehi sebelum pendedahan penganalisa cuaca, PLA asli mempunyai sifat yang baik dari segi sifat tarikan dan sifat tekanan dan tidak pada sifat kekenyalannya.

Kata kunci: Acid Polilaktik, Nanokomposit Asid Polilaktik, Analisa Cuaca, Keupayaan Terbiodegradasi

CHAPTER ONE

INTRODUCTION

1.1 Research Background

Polymers have extremely high molecular weight compound made up of a large number of monomer (called simpler molecules). The process which is linked all the monomers together to form polymer is called polymerization. Monomer can have one or more substituted chemical groups. Variation of chemical groups can affect the chemical and physical properties of the polymer such as solubility, flexibility, strength, stress crystallized, thermally crystallized and etc. There are organic polymer and inorganic polymer in this world.

Since ten years before, nanocomposite based nano-layered silicates have attracted much attention due to its low cost, the availability ad non-isometric structure that derived from a high aspect ratio. Nowadays, conventional composite which is microcomposite is still used. Previous research has proved that nano-layered silicates in the polymer matrix significantly increase strength and heat resistance meanwhile decrease in gas permeability and flammability. However, good dispersion of organoclay in the polymer is crucial to achieve the improvement manner of polymer nanocomposite (Johanne *et. al.*, 2005). The intimate enclosure of nanoparticles in the polymer matrixes can change the properties of materials. The nanoparticles can serve as matrix reinforcement as well as transformation of material properties such as mechanical, chemical and morphological can be achieved. Nowadays, there are many researches based on the development of the polymer nanocomposite (Ujhelyioova, 2007).

Polymer degradation and erosion play crucial role for all polymer. The differences between degradable and non-degradable polymers is, hence, not clean-cut and is in fact arbitrary, as all polymers degraded. It is related on the time scale of degradation and the time scale of the application to compare the degradable and non-degradable polymers. Commonly known that degradable is refer to materials which degrade during their application or immediately after it while non-degradable require a substantially longer time degraded. Actually, the right definition of degradation is the chain scission process during polymer chains are cleaved to form oligomers and finally formed monomers. Meanwhile, erosion describes the loss of materials owing to monomers and oligomers leaving the polymer (Gopferish, 1996).

To improve the quality of polymer microcomposite, technology changes it into polymer nanocomposite. Polymer nanocomposite is the combination of one or more different components of nano-filler in order to obtain the desired properties of polymer composites. Nanoparticles are usually used as filler in polymer matrix nanoclay, metal, carbon nanotubes and etc. The development of polymer nanocomposite is speedily developed as a multidisciplinary research activity. The findings will resulted with a wide application to great benefit of many different fields (Gavitua *et. al.*, 2008).

Polylactic acid (PLA) usually is produced from corn, starch and sugarcanes. PLA derives from the polymerization of the lactide or lactic acid, which is a monomer produced in mammalian muscles during glycogenolysis and correlated with the Kreb cycle through piruvic acid and acetyl coenzyme (CoA) (Fambri, 1996). Meanwhile, lactic acid has different grade which is varying in purity depending on their application. PLA is a biodegradable polymer (Henton *et. al.*, 2005). PLA is not an acid but it is aliphatic polyester derived from renewable resources. Although PLA has been known for more than a century, it has a commercial interest in recent years because it's biodegradable properties (Farrington *et. al.*, 2005).

This type of biopolymer is quite useful for nowadays. In the future outlook, PLA has potential to replace petroleum based plastic. It is regarding to its biodegradable properties. Their degradation occurs with simple hydrolysis of the ester bonds in an aqueous environment. Micro-organisms are metabolised the polymer chain into carbon

dioxide and water as products. So that, if it used for biomedical field, there is no subsequent surgery to remove the implant. Hence, biodegradable polyesters are indicated for various devices, such as plates, pins and screws in bone, as well as for membranes for cell cultures and guided regeneration in soft tissue (Duek *et. al.*, 1998).

Usually, biodegradation studies are carried out in soil or compost, in particular, these materials may enhanced degraded in the presence of compost, a complex biological environment in which microbial diversity is relatively high. Therefore an increased degradation potential for polymeric compounds may result from the research (Kumar, 2010). However, biopolymer like PLA is not a danger material because it constituent passes into the environment (Pagga, 1997). PLA is being preferred alternative to its homologous poly (glycolic acid), due to its slow degradation rate (Fambri *et. al.*, 1996). Rudeekit *et. al.* (2008) also stated that PLA offer a possible alternative compared to the conventional non-biodegradable polymer especially when they are being recycled, it is non-economic.

To obtain toughened products, blending PLA with the other polymers presents a practical and economic measure. Blending PLA with other biodegradable polymers can retain the integrity of biodegradability is particularly interesting (Jiang, 2007). The degree of crystallinity of PLA depends on many factors such as molecular weight, thermal and processing history, temperature and time of annealing treatments (Fambri, 1996). Natural fibres have many benefits rather than synthetic fibres such as low weight, recyclable and biodegradable. Other than that, they are renewable and relatively high strength and stiffness besides cause no skin irritation (Oksman *et. al.*, 2003).

1.2 Problem statements

PLA microcomposite is usually used because of its biodegradability properties however biodegradation of PLA microcomposite is very low in toughness and it is brittle and stiff polymer with low deformation at break. Therefore, PLA nanocomposite is introduced to overcome those weaknesses.

1.3 Research objective

1.3.1 To study on the biodegradable properties of PLA based on organoclay

1.4 Scopes of research

In order to prove the improvement of characteristics of PLA, the scope of research is focusing on:

1.4.1 To produce PLA nanocomposite by melt intercalation method

1.4.2 To characterize PLA nanocomposite by Scanning Electron Microscopy (SEM) and X – Ray Diffraction Analysis (XRD)

1.4.3 To study on the biodegradable properties by using accelerated weathering testing

1.4.4 To study on the mechanical properties by using the tensile strength testing

1.5 Significance of research

PLA is produced from renewable resources has received much attention on their biodegradable properties in research of alternatives biodegradable polymer. PLA is one of the biopolymer that is, nowadays it is one of the most promising biodegradable polymers. In PLA principle, it can also be used as a matrix material in composites. Polymerization of lactic acid into PLA produces biodegradable thermoplastics polyester with good biocompatibility and mechanical properties, such as high tensile strength, thermoplasticity and fabricability. Nowadays, PLA is being developed into a variety of products included food packing, medical tubes, plastic bags of household, biodegradable agriculture films, biomedical application such as drug delivery system and controlled release matrices for fertilizers, pesticides and herbicides. Other than ecological concerns, PLA have resulted that resumed interest in renewable resources based products. In contrast, PLA fiber is derived from annually renewable crops, it is

100% compostable and its life cycle potentially reduces the Earth's carbon dioxide level. PLA are produced from renewable resources, it is by fermentation of carbohydrate. There has some contribution of PLA for environment because PLA is classified as an environmentally friendly polymer (Averous *et. al.*, 2008).

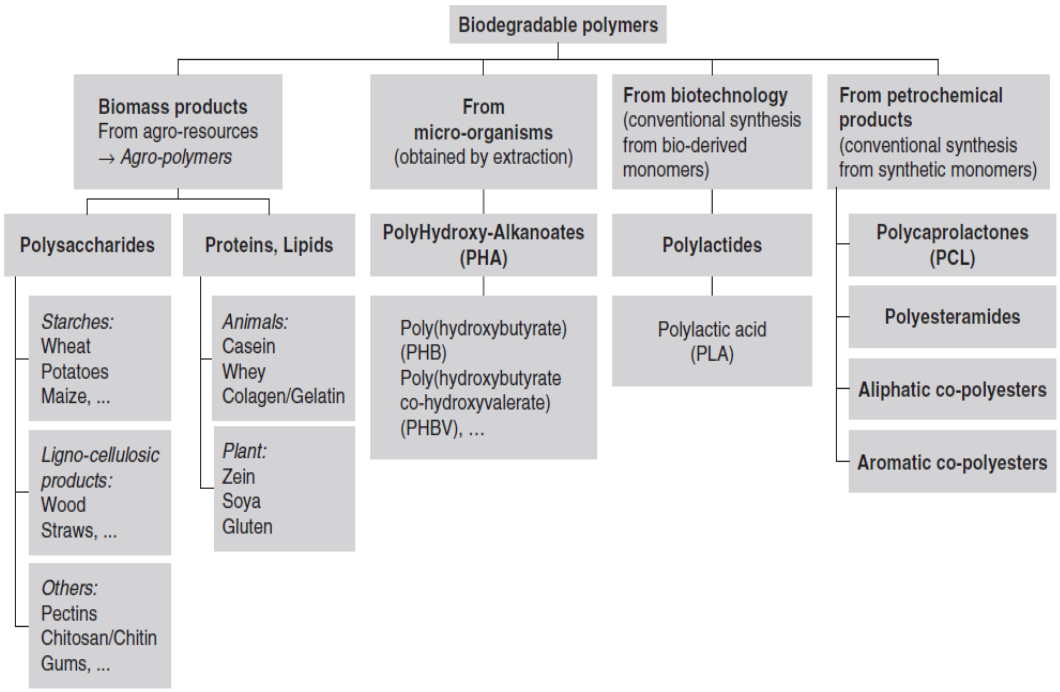

Figure 1.1: Classification of biodegradable polymer (Avérous, 2008)

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Polymer is made up of a large number of monomer and polymers could be divided into two categories: (1) matrix polymer and (2) natural polymer. A matrix polymer is a man-made polymer, while natural polymer is generated from chains of amino acids. A bio-composite is usually consisted of biodegradable polymers as host polymer and natural fibre as reinforcement filler. A polymers matrix and natural fibre are often used as reinforcement due to their good mechanical, chemical and natural properties.

2.2 Polymer

Natural polymer could be produced from natural resources such as starch, corn, cellulose, protein and etc. Polyethylene, polyester, polystyrene, nylon and etc are some of the example for synthetic polymers. However, a synthetic polymer is the most used by industrial and human due to the wide range of consumerism spectrum. A synthetic polymer is categorized into thermoplastic polymer and thermosetting polymer. The difference characteristic between thermoplastic polymer and thermosetting polymer is described in the table 2.1 below:

Table 2.1: Differences between thermoplastic polymer and thermosetting polymer

Thermoplastic polymer	Thermosetting polymer
Become soft when heated and hardens when cooled	Harden permanently when heated
High molecular weight polymers and consist of long molecular chains with no regular structure	Harder, more dimensionally stable, and more brittle
Weak Van der Waals forces	Cross-linked in a curing reaction which produces covalent bonds between them

A copolymer is polymerized from an intimate solution of different types of monomers. A copolymer is divided into three types of chain arrangement; block copolymer, blend/random copolymer and graft copolymer. A block copolymer is a constant pattern combination of polymeric components along a single carbon bonded chain and in contrast blend/random copolymer demonstrate a random mixture of polymeric molecules. The last structure arrangement of copolymer is a graft copolymer. In the graft copolymer arrangement type, component monomers with different chemical compositions are branched out from the primary chain (Xie *et.al*, 2003).

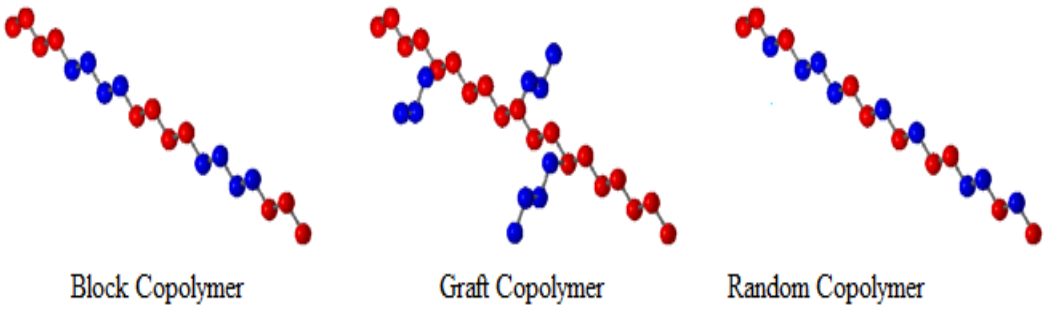

Figure 2.1: Different types of copolymer (Xie *et.al*, 2003)

2.3 Lactic acid

The lactic acid (LA) component of PLA is synthesised by using 100 % renewable resources through a fermentation process. In general, a PLA would degrade if exposed to the environmental setting at rapid rate. The excessive products of the degradation process possess very low toxicity since the products it selves are carbon dioxide and water (Blackburn *et.al*, 2005).

LA is one of the versatile polymers since LA is widely used as flavour and preservative in pharmaceutical, leather, food as well as in textile industries. LA is also used as for the production of base chemical and also polymerization to PLA. The production of the LA are recorded annually at about 80, 000 tonnes per year. At approximately 90% of PLA were produced via LA bacterial fermentation while the rest of PLA production is employed by using hydrolysis approach of lactonitrile (Karin *et. al.*, 1999). LA could be presented as the L-stereoisomer or D-stereoisomer.

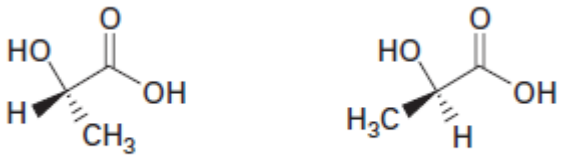

Figure 2.2: The stereoisomers of lactic acid (Farrington *et. al.*, 2005)

Lactic acid commercially produced by the bacterial fermentation of carbohydrate, using homolactic organism, for instance various optimized or modified strains of the genus *Lactobacilli.* The most of simple sugars that produced from agricultural by products also can be used. Amongst of the simple sugars are (1) glucose, maltose and dextrose gain from corn or potato starch (2) sucrose from cane or beet sugar and (3) lactose from cheese whey. Batch processing method is used to conduct the commercial fermentation, which takes three to six days to be completed (Garlotta, 2002).

Farrington *et. al.* (2005) summarized from the published study that energy from the sun is directly promotes photosynthesis mechanism by consuming carbon dioxide (CO_2) and water (H_2O) from the atmosphere and later is converted into starch. An enzymatic hydrolysis is used to extract the starch from the plant cells and consequently altered into a fermentation sugar after an enzymatic hydrolysis. The production of LA from renewable resources through fermentation could be described in the following steps: (1) pre-treatment of substrate including hydrolysis to sugar, (2) fermentation of sugar to LA, (3) separation of bacteria and solid particles from the broth (4) purification of LA.

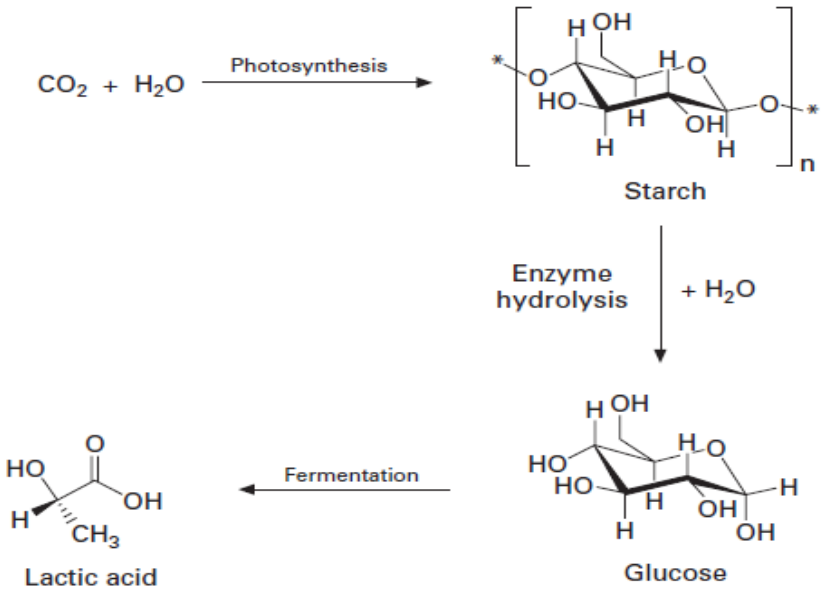

Figure 2.3: Production of lactic acid from renewable resources (Farrington *et. al.*, 2005)

2.4 Polymer nanocomposite

Polymer nanocomposite is defined as nanoparticles polymer bonded in order to produce an advanced materials properties. It has been known in existence for hundred years but is only used commercially nowadays (Butschli, 2004). A polymer nanocomposite is obtained by dispersing nanofiller particles into polymer matrix. PLA is produced through ring opening polymerization of lactides and lactic acid monomers themselves are obtained from the fermentation of sugar feed stocks (Chin, 2005).

The most common filler are utilized in the fabrication of nanocomposite is a clay class material called montmorillonite (MMT). Based on the natural characteristics of clay, it is hydrophilic while polymers are hydrophobic. To make the two components to be compatible, one of the components should be modified to make them interact successfully with each other (Hay, 2000; Ryan, 2003). The alternative way that could be employed to increase the interaction between the organic polymer and inorganic clay by modifying the surface properties of the clay. It can be done by exchanging organic ammonium cations for inorganic cations of the surface of the clay (Sherman, 1999).

There are many types of nanofillers that are commercially available according to market demand. There are carbon nanotubes, graphite platelets and carbon nanofibers. Carbon nanotubes are more expensive organoclay fillers compared to other organoclay fillers that are readily available. Other than that, carbon nanofibers offer excellent electrical and thermal conductivity properties. Southern Clay is the major suppliers for organoclay nanocomposite fibers (Alyssa, 2005).

In order to blend the polymer with nanofiller, there are three common methods; melt intercalation, in–situ polymerization and the solvent method. Melt intercalation process is being done using several machine; extruder, injection moulding and other processing machine. By utilizing in–situ polymerization approach, the filler is added directly into solution of monomer and would be followed by polymerization stage of polymer nanocomposite. In using solvent method, there are three solvents that can be used to undergo this method. The typically used solvents are toluene, chloroform and acetonitrile (Chen, 2004). The melt intercalation method and in–situ polymerization are more commercially used to produce polymer nanocomposite since the solvents method is not environmentally benign.

2.5 Polylactic acid

PLA is a biodegradable thermoplastic polymer with excellent mechanical properties that could be produced on a large scale beginning from fermentation of corn to produce lactic acid and subsequent polymerization process to synthesizing PLA. Most studies about the degradation of PLA are focused on abiotic hydrolysis due to the

established role of PLA as biomedical implants (Shogren *et.al*, 2003). PLA could be either semi-crystalline or totally amorphous due to the characteristic of PLA as aliphatic polyester. It depends on the stereopurity of the polymer backbone. Other than that, PLA also is a unique polymer because it can perform like polyethylene terephthalate (PET), polypropylene (PP) and also polyolefin (Henton *et.al*, 2005).

Degradation occurs in two stages, whereas the first stage is diffusion of water into the polymer; hydrolysing the ester bonds and lowering its molecular weight followed by intracellular uptake of lactic acid into oligomers and humus. Li *et. al*. (1990) found that the carboxylic acid concentration was higher and hydrolysis process is occurred faster in the internal of a sample than on the outer surface due to leakage of the acidic PLA oligomers into the aqueous medium.

PLA has potential and is the most promising biodegradable polymer currently available in the market demands. PLA is a versatile polymer made from natural resources and renewable agriculture raw materials (Yusof, 2010). Moreover, PLA is used mainly to sustain the release of biologically active compounds and in the medical field; PLA is employed for the coating of a wide variety of therapeutic molecules (Onyari *et.al*, 2008).

Non-biodegradable polymers are normally disposed by incineration and as a result would release a large amount of carbon dioxides to the atmosphere. Besides that, it will contribute to global warming and content of toxic gases to the earth. That is the reason why the development of green polymeric materials that would not contribute to the pollution of the environment through toxic or noxious components, which are presence during the manufacturing process. The advantage offered by green labelled polymer is the biodegradability property which means that the degradation mechanism is succeeded through composting process. Although, in order to protect our environment to be in a good condition for our next generation, PLA has increased the commercial interest because it is one of the biodegradable polymers and it can be renewed (Suprakas *et. al*., 2003). The production of PLA is formed either by (1) direct condensation of lactic acid or (2) via a ring opening process.

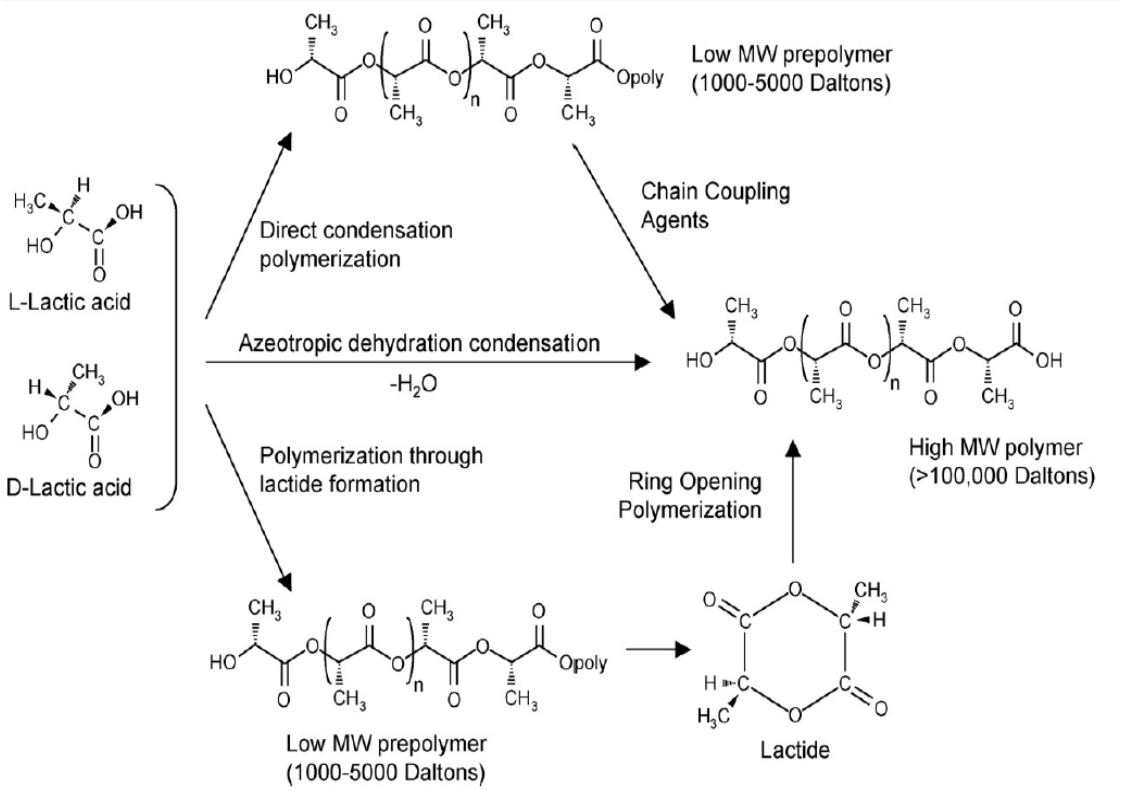

Figure 2.4: Synthesis of PLA from L-lactic acid and D-lactic acid (Auras *et. al.*, 2004)

Table 2.2: PLA properties and characteristic

Properties	**Characteristics**
Density (g/cm^3)	1.33
Melting Point (^oC)	169
Transition Glass (^oC)	45
Crystallization Temperature (^oC)	70 – 120
Crystallinity	0 – 1
Tensile Modulus (MPa)	2980
Tensile Yield Strength (MPa)	25.9
Tensile Elongation at Break (%)	8
Notched Izod Impact (J/m)	144
Flexural Strength (MPa)	44
Flexural Modulus (MPa)	2850
Thermal Conductivity (cal/cm sec ^oC)	Amorphous 3.1×10^{-4} Crystalline 4.5×10^{-4}
Specific Heat (cal/g ^oC)	Below T_g 0.29 Above T_g 0.51
Rockwell Hardness	84 – 115
Biodegradation (%)	100
Water Permeability	172
Surface Tension	50 N/m 37 gd 13 gp

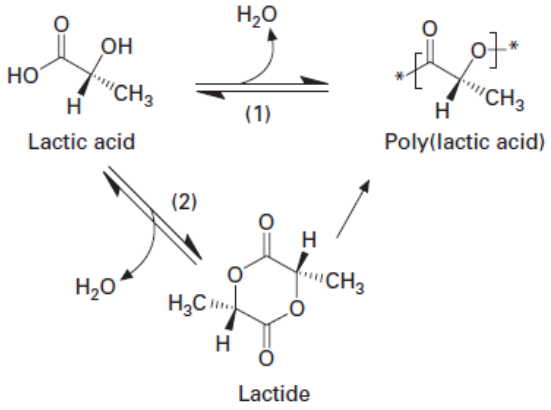

Figure 2.5: Direct condensation of lactic acid (Farrington *et. al.,* 2005)

Polycondensation of lactic acid process was discovered in 1932 by Carothers. It was about the ring opening polymerization of lactide. Then, the discovery has been continued by DuPont who improved purification techniques in 1954. The polycondensation process involves removing water by condensation. The used of solvent under high vacuum and temperature mainly due to the difficulties of removing water and impurities. This production is only for low to intermediate molecular weight polymers. The disadvantages of this process is usually involving large scale of reactor, requires evaporation process, recovery of the solvent and increased colour and racemisation (Garlotta, 2005)

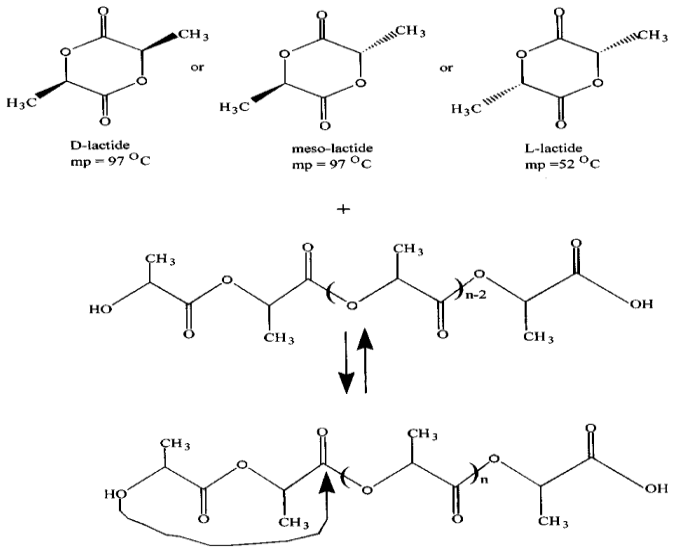

Figure 2.6: Lactide in formation (Garlotta, 2002)

Lactide purification is accomplished by vacuum-distillation of high temperature. After vacuum-distillation of L-lactide, ring opening polymerization resulting high molecular weight PLA with controlled optical and crystal purity. This method can be carried out using melt or solution intercalation method by cationic, anionic and coordination mechanism. Most method has focused on the ring opening polymerization to attain high molecular weight of PLA. This is due to the process is using high boiling point solvent to enforce removing water molecules in direct esterification process. The process is producing cyclic intermediate lactide dimer. It based on removing water components under milder condition. This monomer is ready to purify under vacuum-distillation. Production of cyclic lactide dimer will resulted three potential forms: the D,D-lactide (called D-lactide), L,L-lactide (called L-lactide) and the last one the D,L-lactide or L,D-lactide (called meso-lactide). The meso-lactide is not active because it has different properties (Jamshidian *et. al.*, 2005)

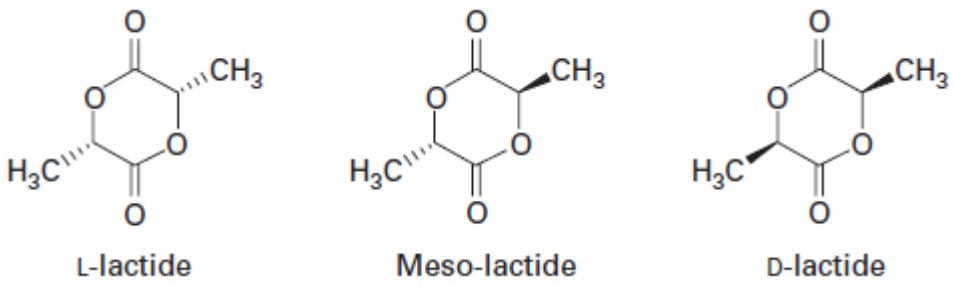

Figure 2.7: Dimer lactide isomers (Farrington *et. al.,* 2005)

Initially, the process is starting with producing low molecular weight pre-polymer PLA by continuous reaction of lactic acid. Pre-polymer PLA then converted into a mixture of lactide stereoisomers, undergo depolymerization using tin catalysis to form ring polymerization to enhance the rate selectivity of the intramolecular cyclization reaction. After ring polymerization is formed, the process is continued by purification process of molten lactide mixture using vacuum distillation. To produce high molecular weight of PLA, the ring opening polymerization is produced by melt intercalation method using a tin catalyst (Farrington *et. al.*, 2005)

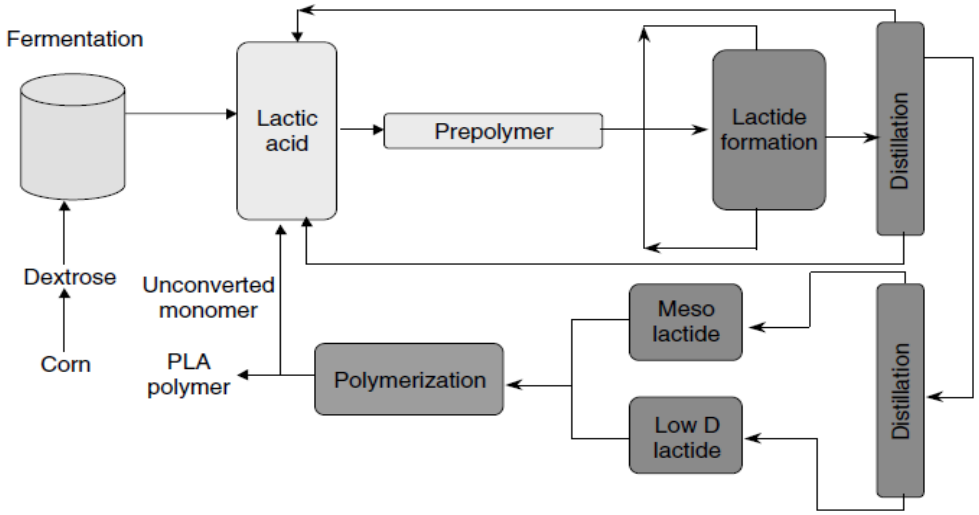

Figure 2.8: Non-solvent process to prepare PLA via prepolymer and lactide (Farrington *et. al.*, 2005)

2.6 Organoclay nanocomposite

Nanocomposite has same meaning with nanoparticles, which mean ultrafine particles in the size of nanometer order. 'Nano' is a prefix introducing the ninth power of ten, which is namely one billionth. Nanoparticles definition is wide; it is depending upon the materials, fields and application concerned. Features of nanoparticles are divided into two. It can be classified into activation of particles surface and increase of surface area. For activation of particles surface, all types of solid consist of atoms or molecules. As atoms and molecules are in nano-sized, they are affected on the materials characteristic and the properties are varies from those bulk solid of the same materials. Generally if the surface area is increased, it is proportionally reversible to the particle size (Hosokawa *et. al.*, 2007).

For instance, organoclay nanocomposite, calcium carbonate, calcium phosphate and hydroxyapatite are some examples of mineral fibres that usually used in industrial sector. Its purpose is to enhance the properties of polymer. There are many types of organoclay nanocomposite or montmorillonite (MMT) that commercially used as filler for preparing polymer nanocomposite. One common type of MMT is bis–(2–hydroxyethyl) methyl tallowakyl ammonium cations or Cloisite B30. The used of

Cloisite B30 has been proved by its ductility properties and polymer nanocomposite processing behaviour. Cloisite B30 tends to improve the surface characteristic, enhanced the crystallinity and at the same time raises the thermal behaviour of polymer nanocomposite. In other word, Cloisite B30 yields the best result in term of thermal stability and inter-galleries spacing dispersion between nanoclays (Paul, 2009).

Lewitus *et. al*. (2006) stated that, polymer nanocomposite based on organoclay layered have a great deal attraction because they exhibit improvement of physical properties if compared to the conventional pristine polymer. These improvements including enhanced of tensile modulus, increased of strength, toughness, heat resistance and gas retardancy, decreased permeability of gas and increased the degradation of polymer nanocomposite. Absence of organoclay layered relatively resulting poor tensile modulus as compared to the pristine polymer. Cloisite B30 is modification of natural MMT with quaternary ammonium salt. It functions as an additive to improve the various physical properties for plastics and rubbers.

Table 2.3: Properties of Cloisite B30 (Southern Clay Inc.)

Properties	**Characteristics**
Commercial name	Cloisite B30
Organic modified	Methyl, tallow, bis – 2 – hydroxyethyl, quartenary ammonium (MT2EtOH)
Modifier concentration	90 meq/100 clay
Moisture	< 2 wt%
Density	1.98 g/cm^3
Color	Off white
X – ray data	d_{001} = 18.5 Å

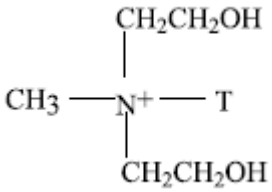

Figure 2.9: Cloisite B30 chemical structural formula (Jiru *et. al.*, 2005)

Type of modified organoclay, Cloisite B30 and type of unmodified organoclay, Cloisite Na^+, were employed as inorganic phase. The polymer nanocomposite strength in the presence of Cloisite B30 was higher than the system of I.30 TC. This is due to the reduced of the chain mobility with introducing of Cloisite B30. In the other hand, the compatibility of Cloisite B30 with the matrix is better than I.30 TC. It is due to the hydroxyl group in the surface modifier, which is allowed better exfoliation to occur with the same amount of nanoclay concentration. It results the enhancement of the materials intensiveness based on Cloisite B30 as filler (Jiru *et. al.*, 2005).

2.7 Polylactic acid nanocomposite

The distribution of organoclay in PLA nanocomposite is proven to be well dispersed without introduce compatibilizing agents. This is due to the interaction of hydrogen bonding between ammonium groups in the inorganic 'surfactant' of the organoclay with the carbonyl group of PLA chain segments. There are also strong interactions between the PLA hydroxyl ends group and MMT platelet surfaces or the organically modified MMT, the hydroxyl groups of the ammonium surfactant (Balakrishnan *et. al.*, 2010).

The presence of organoclay represents as nucleation site. The nucleation site is function to ease the crystallization process of PLA. It produced small crystallites and lowers the crystallinity. Crystallinity controls the unique skin-core foam morphologies in PLA and PLA nanocomposite. Organoclay nanocomposite provides nucleation sites to generate foam morphology in PLA nanocomposite with high crystallinity (Liao *et. al.*, 2011)

2.8 Type of nanocomposite

Jiang *et. al.* (2007) defined that, to prepare polymer nanocomposite, it must use a co–rotating extruder equipped. The extruder with a gravimetric feeder and compound a strand of pelletizes of mixed polymer and organoclay. The temperature of the barrel of the extruder must be controlled properly to make sure the product yield of the polymer nanocomposite produce is in a well mixing composition. Before extrusion process, the pristine polymer and organoclay should be dried first to release the moisture trapped in the materials. The mixture of polymer and organoclay fed into the gravimetric feeder of extruder to melt compounding the materials. The extrudate is cooled in a water bath temperature and granulated by a pelletizer. Then, the compounded will be fed into injection molding to form desired shape.

The types of polymer nanocomposite are depending on the strength interfacial interactions between the polymer matrix and organoclay layered. The organoclay layeree that properly dispersed creates much higher surface area throughout the polymer matrix. There have three different types of dispersion of organoclay nanocomposite. It is intercalated nanocomposite, phase separated nanocomposite and exfoliated nanocomposite (Suprakas, 2003).

In figure 2.10 represents main types of nanocomposite structure for layered silicate materials. Phase separated nanocomposite structure will be obtained if the silicate sheets could not be penetrate between polymer matrix. The properties stay in the same range as dispersion in microcomposite. In an intercalated nanocomposite structure, silicate layers are dispersed between extended polymer chains. This will result a well-ordered multilayer morphology with alternating polymeric and inorganic layers. If the silicate layers are completely and constantly dispersed between the polymer matrixes, an exfoliated structure nanocomposite is obtained. The resultant of nanocomposite structure are significantly varies regarding to the physical properties (Hussain *et. al.*, 2006).

2.8.1 Intercalated nanocomposite

The insertion of organoclay structure into polymer matrix occurs in a crystallographically regular feature, regarding to the organoclay to polymer ratio. Normally, intercalated nanocomposite is interlayer by a few layers of organoclays between polymer matrixes. The properties of this type is typically resemble of ceramic tone (Suprakas *et. al.*, 2003).

2.8.2 Phase separated nanocomposite

Conceptually of this type of nanocomposite is almost same as intercalated nanocomposite structure. In addition, sometimes organoclay layers gather due to hydroxylated edge/edge intercalation (Suprakas *et. al.*, 2003).

2.8.3 Exfoliated nanocomposite

Exfoliated nanocomposite is a type of dispersion of organoclay nanocomposite that the organoclay layered structure is separated in a continuous polymer matrix that depends on organoclay loading by an average distance between organoclay and polymer matrix (Suprakas *et. al.*, 2003).

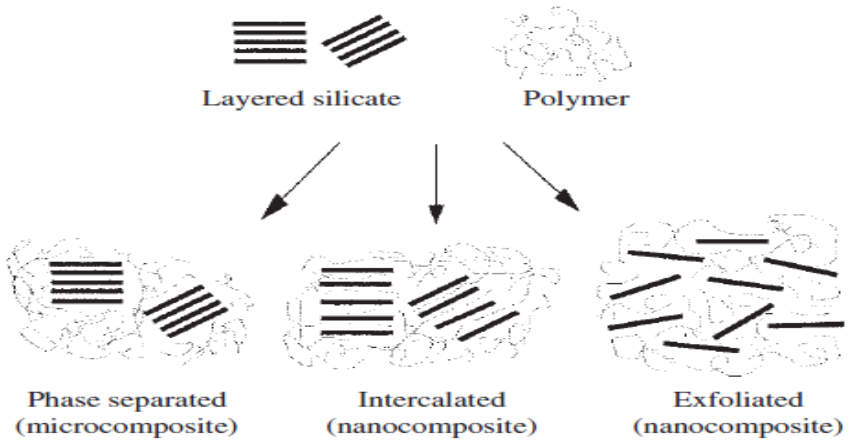

Figure 2.10: Scheme of three main types of layered silicates in polymer matrix (Hussain *et. al.*, 2006)

2.9 Type of intercalation polymerization

Intercalation polymerization is a method to mix together the polymer materials and organoclay nanocomposite. It has been successfully proven to synthesis polymer nanocomposite. The intercalation polymerization has been divided into three methods regarding to the processing techniques.

2.9.1 In-situ intercalation polymerization

In–situ polymerization is dispersion of organoclay which is called silicate layered particles. The silicate layered particles at first are dispersed in polymer matrixes and the mixture is polymerized. Typical silicate layered particles are commonly used is clay minerals such as MMT or originally large kaolin. Many laminated layers are in nanometers sized are formed by these silicate layered particles (Hosokawa *et. al.*, 2007).

For this type of polymerization, organoclay is swollen within the polymer layers and the polymerization occurs between the intercalated layers. It can be initiated either by heating or radiation. Other than that, it also can be done by diffusion of suitable initiator or by organic initiator or catalyst fixed through cation exchanged inside the interlayer of polymer matrixes before start the swelling step (Bhattacharya *et. al.*, 2008).

2.9.2 Solution intercalation polymerization

Solution intercalation has two processes transportation, namely solvent diffusion and chain disentanglement. In effort to understand the physics of dissolution mechanism of glassy polymers, it has several models that have been proposed for this kind of effort. It can be categorized as phenomenological, external mass transfer, stress relaxation and molecular theories, anomalous transport models and scaling laws and molecular theories in continuum framework. Those approaches have incorporated phenomena as stress relaxation, polymer viscoelasticity and chain disentanglement, anomalous transport of solvent, chain reputation and external mass transfer limitations. Other than that, many experimental techniques have been done to characterize polymer dissolution behaviour and molecular properties of solvent and polymer matrix (Chou, 2002).

In other word, each polymers will soluble in specific solvent for instance chloroform, acetone, dimethyl chloroform, toluene or others meanwhile organoclay layers are swellable between the layers of polymer matrixes. The polymer chains intercalate and organoclay layer displaced the solvent after the mixing process of the polymer chain and organoclay solution is done. Actually this method is well used for non-polar or less polarity of the polymer chains. Silicate layered is facilitates into polymer matrixes and finally formed intercalated layer of polymer nanocomposite (Suprakas, 2003).

2.9.3 Melt intercalation polymerization

Nowadays, melt intercalation polymerization method is the best method amongst other polymerization method. This is due to this type of polymerization is environmental friendly. Melt intercalation polymerization is including blending and annealing process. It is not contain any organic solvents. In addition, melt intercalation polymerization also an economically favourable method for industries from waste perspective. Other than that, melt intercalation is compatible with current industrial process such extrusion and injection molding. This type of polymerization is able to replace other types of polymerization that is not eco-friendly. Melt intercalation leads to make new hybrids that previously inaccessible and it is highly specific for producing polymer nanocomposite (Suprakas, 2003).

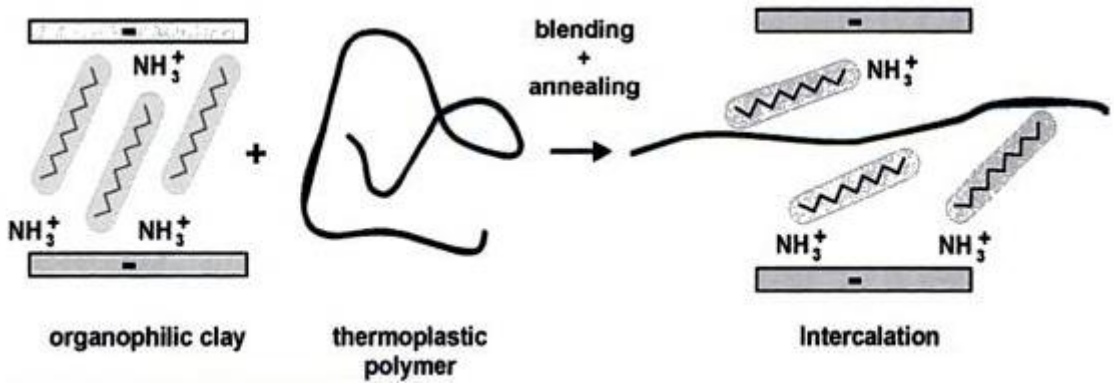

Figure 2.11: Melt intercalation polymerization method (Zaikof *et. al*, 2005)

2.10 Synthesis the samples

The polymer matrix and organoclay are mixed together using extrusion and injection molding. The mix compounds will be press using shear forces to make the compounds dispersed well while formed polymer nanocomposite (Brody, 2003; Chen, 2004).

2.10.1 Extrusion

Before processing, the samples (PLA and organoclay nanocomposite) are dried for duration 24 hours with temperature 90 ^{o}C. The mixed compounds are processed into extrusion machine with five heated zones and die end. The mixed composition ratios were maintained at composition as stated in table 2.4. (Ratto *et. al.*, 1999).

Table 2.4: Designation of materials and their compositions

Compositions	PLA (%)	B30 nanoclay (%)
Pristine Polylactic Acid	100	0.0
Polylactic Acid/B30 nanoclay	99.5	0.5
Polylactic Acid/B30 nanoclay	99.0	1.0
Polylactic Acid/B30 nanoclay	98.0	2.0

The polymer and organoclay is melting while being spun by using a twin screw extruder. This equipment will equipped with a cooling jacket to prevent the mix polymer nanocomposite become flake during melting process along the barrel zones. Initially, polymer spun through a single nozzle circular spinneret. Along the twin screw extruder, there are a few types of spinneret to blend the mixer. The heaters at every barrel are function to supply heat to melt the polymer and organoclay together. Then, at the end of the extrusion, the well mix polymer nanocomposite will be collected on a glass drum (Fambri, 1996).